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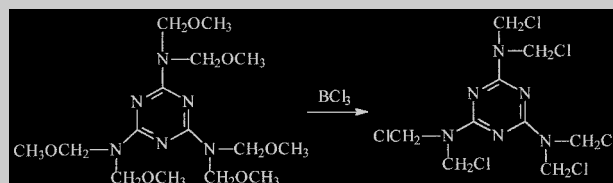
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Communication: Combination of hexa(chloromethyl)-melamine (HCMM) and zinc chloride was found to be a multifunctional initiator system for the living cationic polymerization of isobutyl vinyl ether. HCMM was synthesized by reaction of hexa(methoxymethyl)melamine and boron trichloride. Characterization of the polymers by means of GPC and ^1H NMR showed that initiation was rapid and quantitative and that the initiator is hexafunctional, leading to six-armed star-shaped polymers.



A new multifunctional initiator system for the living cationic polymerization of vinyl ethers

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Introduction

For the synthesis of star-shaped polymers, two methods based on living polymerization have been described^{1–3}: end-capping of linear living polymers with a multifunctional end-capper (“arm-first” method), and initiation of the polymerization with a multifunctional initiator system (“core-first” method). In case of living cationic polymerization of vinyl ethers, star-shaped polymers have been prepared by both methods^{4,5}. The core-first method has the advantage that, at the end of the polymerization, end-capping of the living chain ends is still possible, thus providing an elegant method for the synthesis of star-shaped multi-telechelic polymers.

The classical initiation method for the controlled polymerization of vinyl ethers utilizes activated halides as starting materials^{6,7}. The most used ones are α -iodo- or α -chloroalkyl ethers which are transformed into initiating species by addition of a Lewis acid. In the present paper, we wish to report on another type of activated halide which simultaneously provides the possibility to perform a multifunctional initiation reaction. The new system is based on hexa(chloromethyl)melamine (HCMM) in which the chloride functions are activated by the presence of (non-basic) amino functions in α -position.

Experimental part

Materials

Toluene, CH_2Cl_2 and isobutyl vinyl ether (IBVE) were dried over CaH_2 and distilled just before use. ZnCl_2 solution in

diethyl ether (1.0 M) and BCl_3 in hexane (1.0 M) were purchased from Aldrich and used without further treatment. Hexa(methoxymethyl)melamine (HMMM) (Cymel 303) was purchased from American Cynamide and used without further purification.

Synthesis of hexa(chloromethyl)melamine (HCMM)

A 250 ml double-necked flask provided with rubber septum and magnetic stirring bar containing 4.0 g of HMMM was dried in vacuum at 40°C for 1 h and then filled with dry argon. By means of a hypodermic syringe, 120 ml of CH_2Cl_2 was injected through the septum into the flask and 64.5 ml of BCl_3 solution in hexane (1.0 M) was added dropwise at room temperature under stirring. After addition of the BCl_3 solution, the reaction mixture was stirred for 0.5 h. The mixture was washed with a saturated aqueous solution of NaHCO_3 and a dilute solution of Na_2SO_4 . The organic phase was dried over anhydrous Na_2SO_4 overnight. After removing the solvent under rotary evaporation, 2.88 g of HCMM was acquired as a white powder (m.p. 176°C ; yield: 72%). Elemental analysis is as follows:

$\text{C}_9\text{H}_{12}\text{N}_6\text{Cl}_6$ (416.9)	calc.	C 25.93	H 2.88	N 20.16	Cl 51.02
	found	C 26.80	H 3.31	N 20.08	Cl 46.87

Typical polymerization procedure

To a dry solution of 0.05 g of HCMM in 100 ml of CH_2Cl_2 , cooled at -45°C , a suitable amount of IBVE was added under dry argon. Then, 300 μl of ZnCl_2 solution in diethyl ether (1.0 M) was injected to initiate polymerization. After 2 h, the reaction was terminated with methanol/ammonia or

another functional terminating agent. The mixture was washed with water, the organic phase was dried over anhydrous Na_2SO_4 overnight and the solvent was evaporated. After drying under vacuum, poly(IBVE) was acquired as colorless, transparent and viscous liquid.

Characterization methods

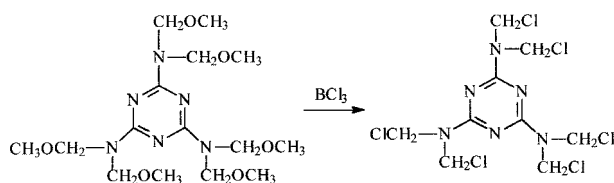
^1H NMR spectra were recorded on a Bruker AC 500 FT. Gel permeation chromatography (GPC) was performed on a 60 cm Pol. Labor. column, 1000 Å porosity, eluant CHCl_3 and calibrated by polystyrene standards. A combination of refractive index detection (Waters 2410) and UV detection at 254 nm (Kontron Instruments HPLC detector 742) was used.

Results and discussion

Synthesis of HCMM

HCMM was prepared by reaction of hexa(methoxymethyl)melamine (HMMM) with boron trichloride (Scheme 1):

Scheme 1:



The formation of HCMM was proven by comparing the ^1H NMR spectrum of the starting material with that of the end product. As shown in Fig. 1, singlets at 3.5 and 5.3 ppm corresponding to methylene and methoxy groups in HMMM have completely disappeared in the end product and are replaced by one singlet at 5.7 ppm, a value that is in good agreement with the structure of HCMM.

Preparation of star-shaped polymers with HCMM initiator

The polymerization of IBVE with HCMM was carried out at -45°C in dichloromethane using zinc chloride as activator. The polymerization reactions were stopped after approximately 2 h by addition of a mixture of an alcohol and ammonia or triethylamine which is expected to produce the corresponding acetal at each chain end that was still active at the moment of termination. Under these conditions, almost quantitative conversions to polymer were obtained. The polymers were analyzed by means of gel permeation chromatography (GPC) using a combination of refractive index and UV detection. Fig. 2 shows a typical GPC analysis of a polymer that was terminated with methanol/ammonia. This chromatogram

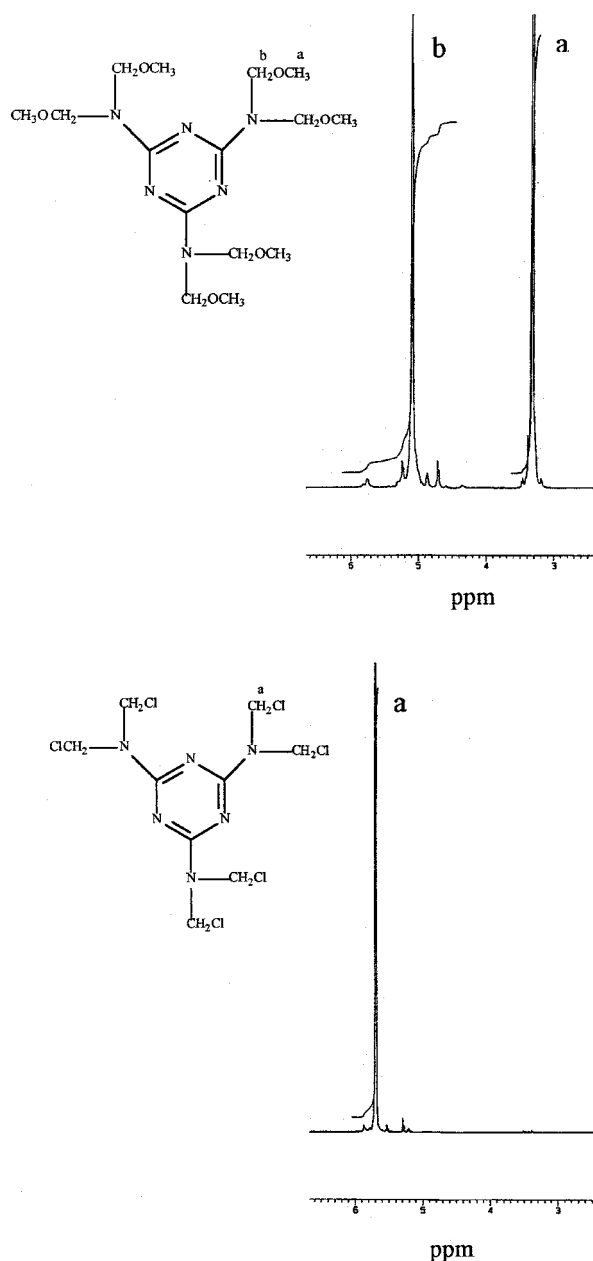


Fig. 1. ^1H NMR spectra of HMMM and HCMM

demonstrates that the polymer shows absorbance of UV light (254 nm), and that the molecular weight distribution of the polymer is unimodal and relatively narrow. This proves that a relatively fast initiation reaction did occur and that the aromatic function originating from HCMM is incorporated into the polymer chain.

A ^1H NMR spectrum of a polymer obtained with benzyl alcohol as terminating agent (Fig. 3) shows that the polymer contains benzylic end groups as evidenced by the peaks at 7.4 (aromatic protons) and 4.75 ppm (benzyl ether methylene protons). The ratio of the area of the benzyl peaks to the area of the methyl peaks (isobutyl groups of the polymer) allows us to calculate the average length

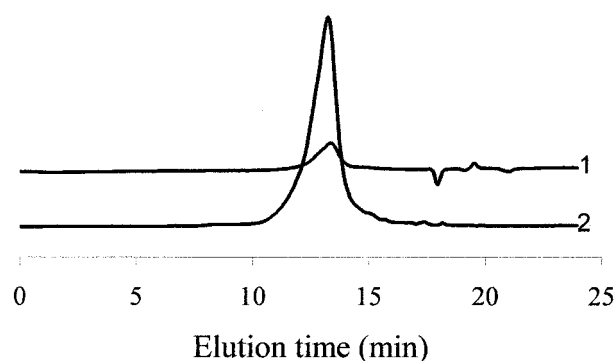


Fig. 2. GPC analysis of star-shaped poly(IBVE) with RI detector(1) and UV detector(2)

of each polymer arm, assuming that all polymer chains were still active at the moment of termination. If the thus obtained values are compared with the values obtained by GPC, it can be concluded that each polymer formed must contain several chain-ends, in other words, the polymers must have a star-shaped structure.

Based on the above mentioned results, the following reaction scheme is proposed (Scheme 2):

Various polymerization reactions have been carried out using different conditions, and typical analytical results are summarized in Tab. 1.

If it is assumed that each HCMM molecule has formed one (star-shaped) polymer molecule, the calculated mole-

Tab. 1. Characterization of poly(IBVE) obtained from HCMM/ ZnCl_2 as initiating system

$[\text{M}]/[\text{HCMM}]$	\bar{M}_n (calc.) ^{a)}	IBVE/ benzyl	\bar{M}_n (arm) ^{b)}	\bar{M}_n (star) ^{c)}	\bar{M}_n (GPC)	\bar{M}_w/\bar{M}_n
68	7650	10.2	1127	6966	4530	1.28
135	14360	21.2	2227	13566	9870	1.32
174	18330	26.2	2727	16566	12910	1.31
286	29535	48.6	4967	30006	22400	1.28

a) $([\text{M}]/[\text{In}]) \times 100 + 846$ (molecular weight of hexa(benzyl-oxy)methyl)melamine).

b) $([\text{IBVE}]/[\text{benzyl}]) \times 100 + 107$.

c) $\bar{M}_n(\text{arm}) \times 6 + 204$.

cular weight of the end product is given by $([\text{M}]/[\text{In}]) \times 100 + 846$ (846 is the sum of six benzyloxy end groups and one hexamethylene melamine central group). These values are given in the second column of Tab. 1. The third column displays the ratio of benzyl end groups to IBVE units in the polymers as measured by ^1H NMR. This ratio leads to the corresponding average degrees of polymerization (DP) of the arms and, after multiplication with 100 and addition of 107 (corresponding to one benzyloxy group) to the \bar{M}_n of the arms. These figures are shown in column 4. \bar{M}_n of the star polymer, assuming 6 arms, is obtained by multiplying the value of column 4 by 6 and adding the mass of the hexamethylene melamine core (204). These values are displayed in column 5. Columns

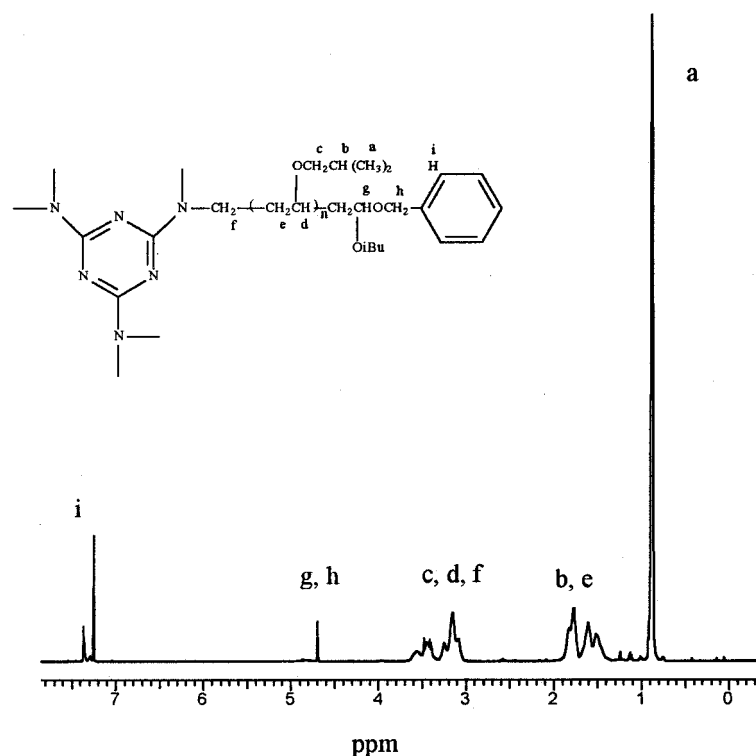
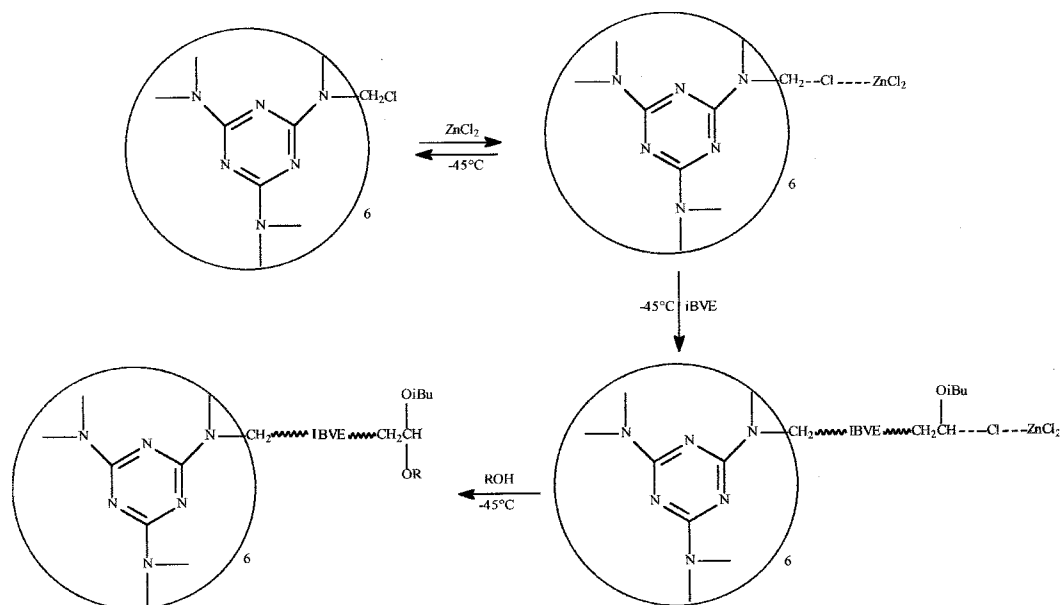


Fig. 3. ^1H NMR spectrum of star-shaped poly(IBVE) with benzyloxy end groups

Scheme 2:



6 and 7 display the experimental GPC results. Calculated values of \bar{M}_n and those obtained from end group analysis, assuming six armed structures, are in reasonable agreement. The experimental values of \bar{M}_n obtained by GPC analysis increase with increasing $[\text{M}]/[\text{HCMM}]$ ratio, as expected for a "living" system, but are systematically somewhat lower than the calculated values. This is in agreement with the star-shaped structure of the polymers. It has been reported⁸⁾ that star-shaped polymers elute at higher elution volumes compared to those of their linear homologues due to their smaller hydrodynamic volume.

Conclusion

Polymerization of IBVE with the initiating system HCMM/ ZnCl_2 at -45°C in dichloromethane leads to six-armed star-shaped poly(IBVE). The resulting polymers are distinguished by controlled molecular weights and relatively narrow molecular weight distributions, confirming quantitative initiation and living polymerization mechanism. Combination of this initiator system with an appropriate end-capping reaction, should provide the pos-

sibility to prepare star-shaped end-group functionalized poly(vinyl ethers).

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